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Dellamorte et al.

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(54) **CATALYST COMPOSITIONS AND METHODS OF PREPARATION AND USE THEREOF**

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B01J 35/51	(2024.01)
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C01G 25/02	(2006.01)
C07C 5/333	(2006.01)

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CPC ***B01J 21/066*** (2013.01); ***B01J 23/10*** (2013.01); ***B01J 35/50*** (2024.01); ***B01J 35/51*** (2024.01); ***B01J 35/612*** (2024.01); ***B01J 35/613*** (2024.01); ***B01J 35/615*** (2024.01); ***B01J 37/18*** (2013.01); ***C01G 25/02*** (2013.01); ***C07C 5/3332*** (2013.01); *C01P 2002/76* (2013.01); *C01P 2006/12* (2013.01); *C07C 2521/06* (2013.01)

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USPC 502/302, 349

See application file for complete search history.

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(57) **ABSTRACT**

Disclosed are methods of dehydrogenating a light alkane gas (and/or light alkene gas), which include adding hydrogen (H_2) to the light alkane gas (and/or light alkene gas) in the presence of a catalyst composition containing zirconium oxide. Also disclosed are catalyst compositions containing zirconium oxide and methods of preparation thereof, where the catalyst compositions are useful in methods of dehydrogenating light alkane gas.

15 Claims, 4 Drawing Sheets

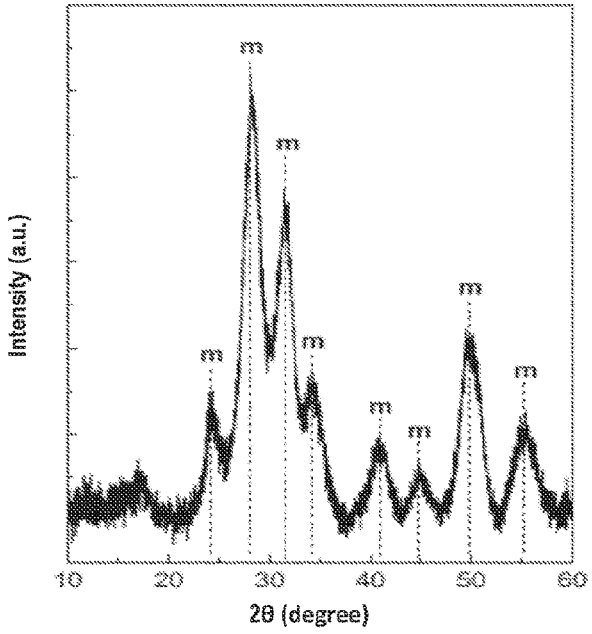

FIG. 1

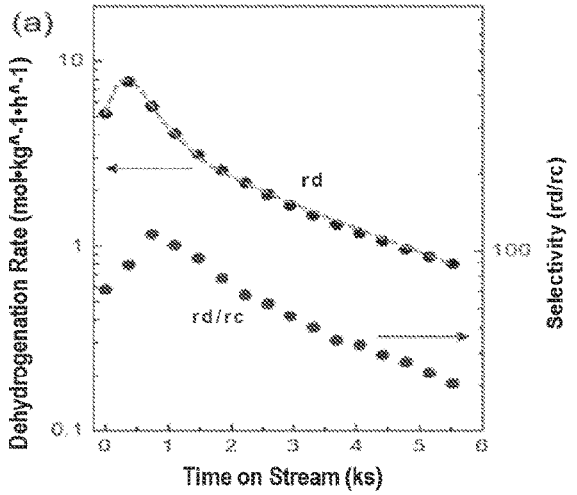

FIG. 2(a)

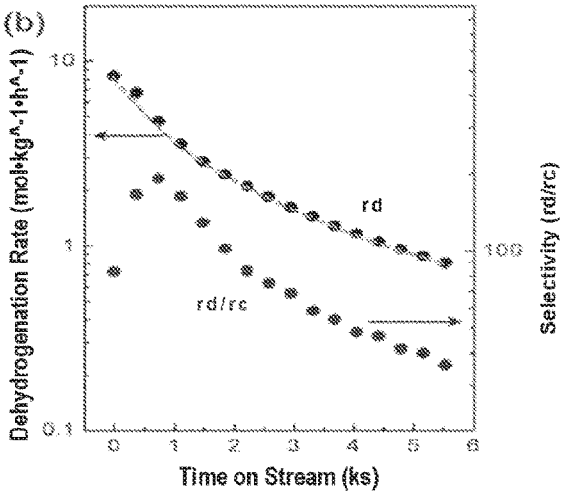

FIG. 2(b)

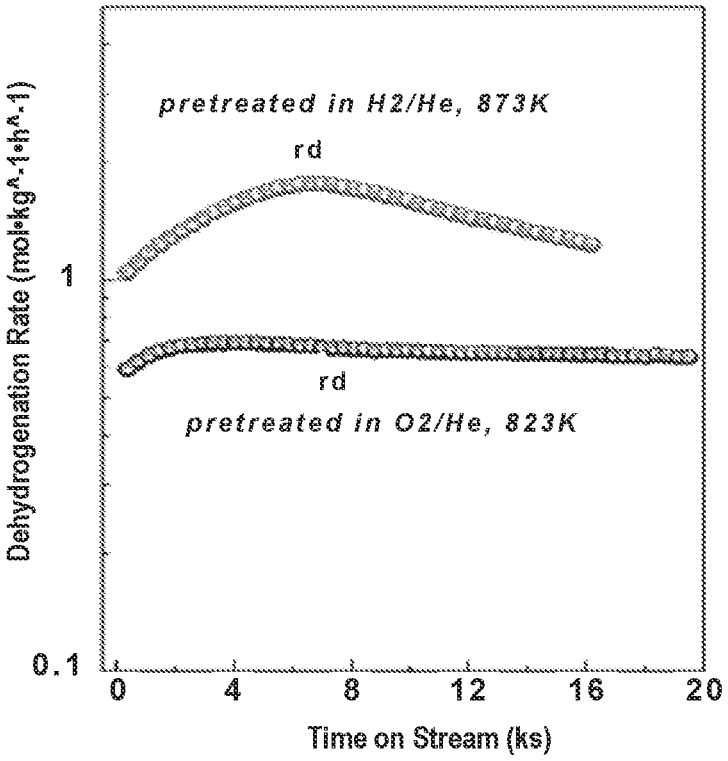
pretreated in H2/He, 873K
rd
rd
pretreated in O2/He, 823K
Dehydrogenation Rate (mol•kg^-1•h^-1)
1
0.1
0
4
8
12
16
20
Time on Stream (ks)

FIG. 3

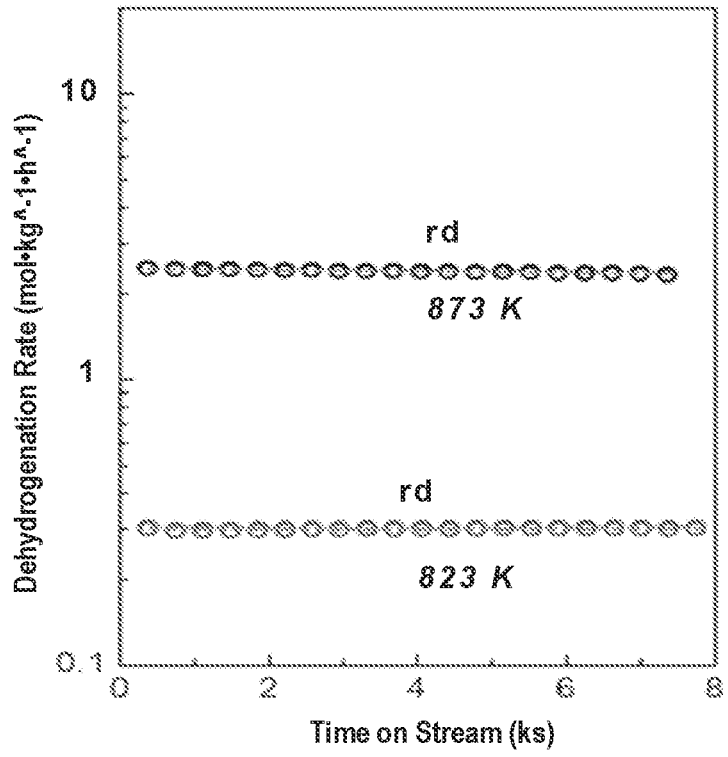
rd
873 K
rd
823 K
Dehydrogenation Rate (mol•kg^-1•h^-1)
10
1
0.1
0
2
4
6
8
Time on Stream (ks)

FIG. 4

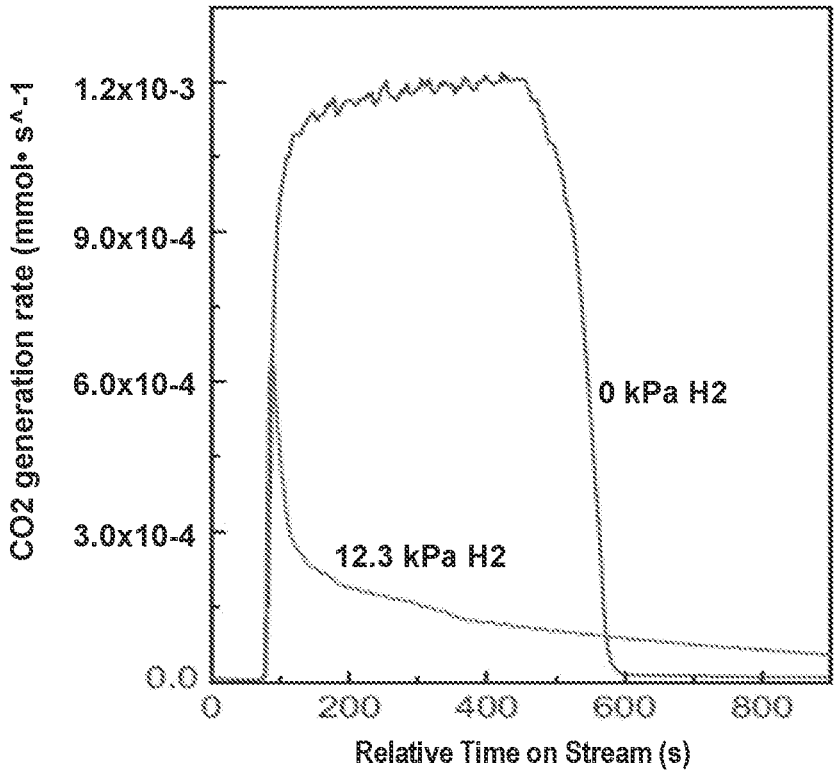
CO2 generation rate (mmol• s^-1
1.2x10-3
9.0x10-4
6.0x10-4
3.0x10-4
0.0
0 kPa H2
12.3 kPa H2
0
200
400
600
800
Relative Time on Stream (s)

FIG. 5

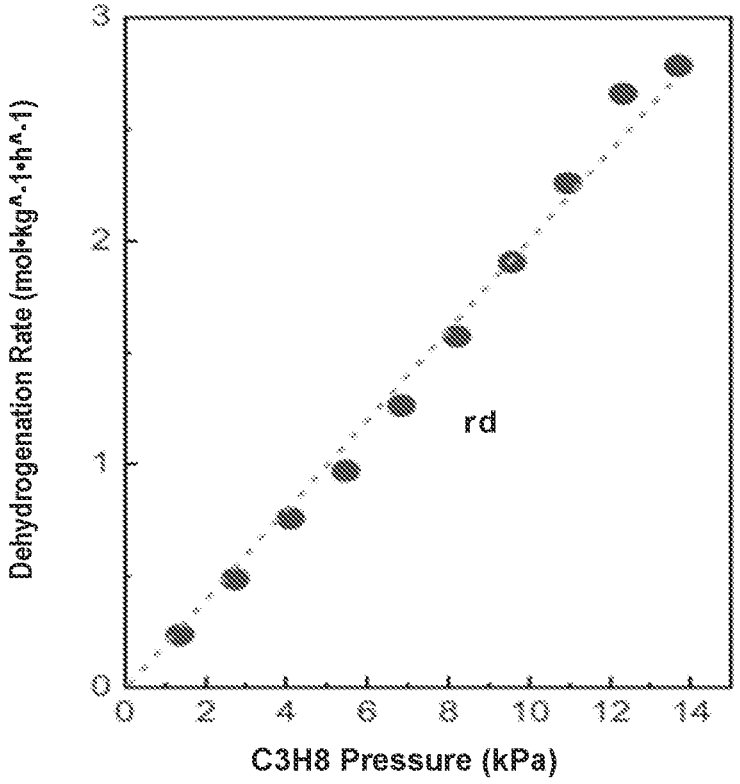
Dehydrogenation Rate (mol•kg^-1•h^-1)
3
2
1
0
rd
0
2
4
6
8
10
12
14
C3H8 Pressure (kPa)

FIG. 6

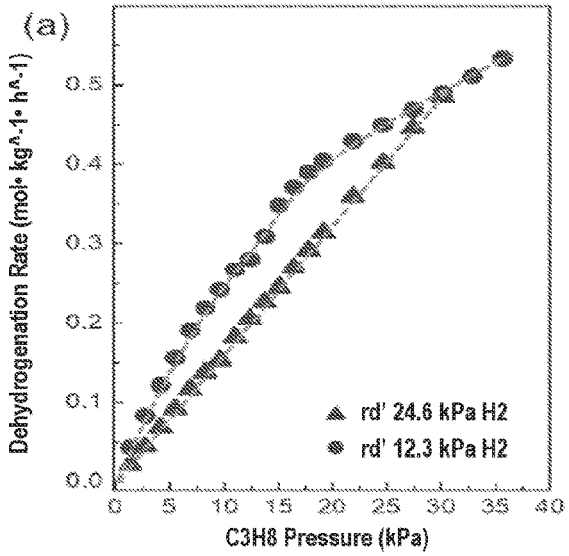

FIG. 7A

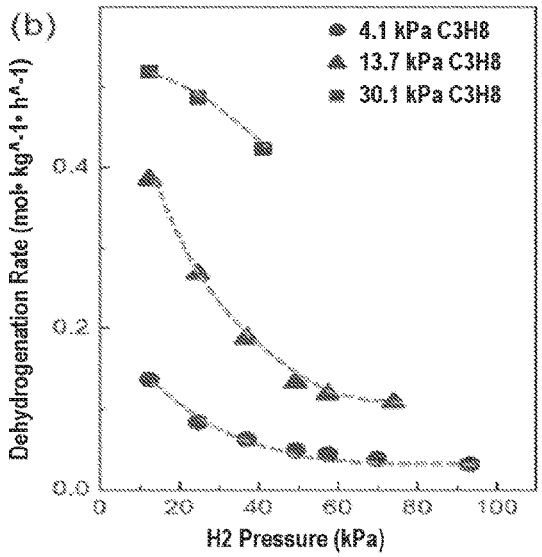

FIG. 7B

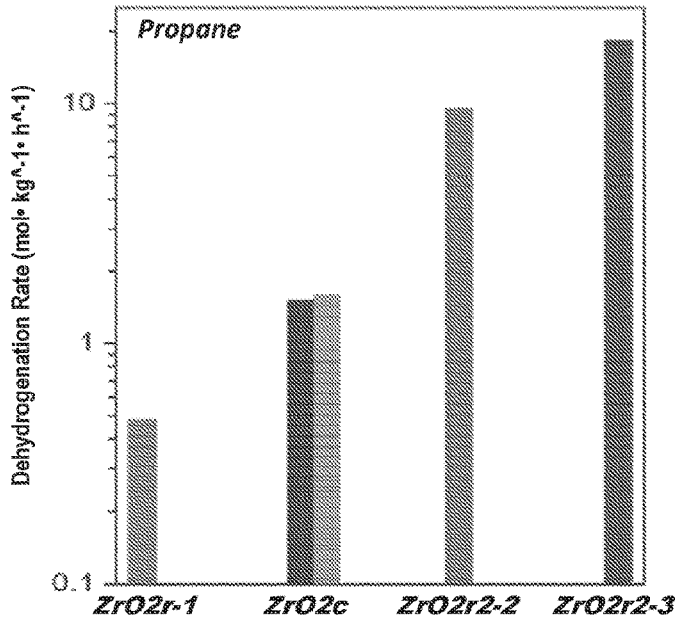

FIG. 8

CATALYST COMPOSITIONS AND METHODS OF PREPARATION AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a national stage entry under 35 U.S.C. § 371 of International Patent Application No. PCT/US2021/017072, filed on Feb. 8, 2021, which claims the benefit of priority of U.S. Provisional Patent Application No. 62/981,655, filed on Feb. 26, 2020, the disclosures of which are hereby incorporated by reference herein in their entireties.

FIELD

This disclosure relates to methods of using catalyst compositions for dehydrogenation of light alkane gas (and/or light alkene gas). The disclosure also relates to catalyst compositions, for example, that can be used in such dehydrogenation reactions and methods of preparation thereof.

BACKGROUND

Catalytic dehydrogenation of alkanes is an efficient conversion technology for the production of alkenes as compared to traditional petroleum-based processes such as fluid catalytic cracking and thermal steam cracking. Traditional processes suffer from high-energy demand, dwindling petroleum reserve and low selectivity toward any particular target alkene. Catalytic dehydrogenation is also more environmentally friendly than oil-based processes because it uses natural gas and shale gas as feedstock, which contain fewer impurities.

Two industrial processes for the production of light alkene using dehydrogenation are 1) the chromia-alumina-based Catofin® process; and 2) the Pt—Sn-based Oleflex™ process. However, the use of chromium (Cr) and platinum (Pt) based catalysts presents environmental and health issues. For example, according to the Occupational Safety and Health Administration (OSHA), human exposure to chromium (V1) (Cr^{6+}) may cause serious health issues such as lung cancer.

Platinum-based catalysts used for dehydrogenation of alkanes can include Pt deposited alone, or in combination with another material such as tin (Sn), on an inactive support. The inactive support can be, for example, a ZrO_2 support that is inactive under the reaction conditions that cause the Pt or Pt—Sn to be active. However, the redispersion of Pt in such catalysts often requires the addition of chlorine-based compounds during the catalyst regeneration process, which is ecologically harmful. Moreover, such Pt-based catalysts are sensitive to trace impurities and very costly.

There is a need for methods and catalyst compositions that inhibit deactivation of the catalyst composition and at same time maintain a considerable dehydrogenation activity. There is a further need for catalyst compositions that are free of Cr and precious metals, such as Pt, and that increase the safety and sustainability of the dehydrogenation process. The use of such catalyst compositions in the dehydrogenation of light alkanes (and/or alkenes) could improve the total yield of dehydrogenation products within one cycle and require less frequent catalyst regenerations.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows an X-ray diffraction (XRD) spectrum of a catalyst composition comprising zirconium oxide (ZrO_2) according to embodiments.

FIG. **2***a* shows the dehydrogenation rate per mass of catalyst (r_d) and the selectivity of the dehydrogenation reaction (ratio between dehydrogenation and cracking rate, r_d/r_c) during a propane dehydrogenation (PDH) reaction on a pretreated ZrO_2 catalyst.

FIG. **2***b* shows the dehydrogenation rate per mass of catalyst (r_d) and selectivity of the dehydrogenation reaction (ratio between dehydrogenation and cracking rate, r_d/r_c) during a PDH reaction on a pretreated ZrO_2 catalyst.

FIG. **3** shows the dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction on a pretreated ZrO_2 catalyst.

FIG. **4** shows the dehydrogenation rate per mass of catalyst with additional H_2 present (r_d) during a PDH reaction on a ZrO_2 catalyst with O_2/He pretreatment at different temperatures.

FIG. **5** shows the CO_2 generation rate during a re-oxidation process after a PDH reaction with and without the presence of additional H_2 at 873 K on ZrO_2 catalyst.

FIG. **6** shows the dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction.

FIG. **7**(*a*) shows the dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction on a ZrO_2 catalyst as a function of C_3H_8 partial pressure.

FIG. **7**(*b*) shows the dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction.

FIG. **8** shows a comparison of initial dehydrogenation rate of propane among ZrO_2 catalysts.

BRIEF SUMMARY

According to various embodiments, disclosed herein are catalyst compositions, comprising zirconium oxide (ZiO_2), wherein the catalyst compositions are free of at least one of chromium and a precious metal (e.g., Pt, gold, silver, copper, palladium, etc.). In embodiments, the catalyst compositions are free of chromium and platinum.

Further disclosed herein, according to various embodiments, is a method of preparing a catalyst composition, comprising combining $ZrO(NO_3)_2xH_2O$, water and urea at a temperature of about 20° C. to about 25° C. to form a $ZrO(NO_3)_2$ solution; and crystallizing the $ZrO(NO_3)_2$ solution at an elevated temperature under an autogenous pressure for about 2 h to about 36 h to form the catalyst composition.

According to further embodiments, disclosed herein is a method for dehydrogenating a light alkane gas (and/or a light alkene gas), comprising: combining hydrogen (H_2) with the light alkane gas (and/or light alkene gas) in the presence of a catalyst composition comprising zirconium oxide (ZrO_2).

DETAILED DESCRIPTION

Described herein are methods of using catalyst compositions for the dehydrogenation of light alkane gases (and/or light alkene gases). Also disclosed are catalyst compositions for such dehydrogenation reactions and methods of preparation thereof. It is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in a variety of ways.

Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with

the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases such as "in one or more embodiments," "in certain embodiments," "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

As used herein, the singular forms "a," "an," and "the" include plural references unless the context clearly indicates otherwise. Thus, for example, reference to "a catalyst material" includes a single catalyst material as well as a mixture of two or more different catalyst materials.

As used herein, the term "about" in connection with a measured quantity, refers to the normal variations in that measured quantity as expected by one of ordinary skill in the art in making the measurement and exercising a level of care commensurate with the objective of measurement and the precision of the measuring equipment. In certain embodiments, the term "about" includes the recited number 10%, such that "about 10" would include from 9 to 11.

The term "at least about" in connection with a measured quantity refers to the normal variations in the measured quantity, as expected by one of ordinary skill in the art in making the measurement and exercising a level of care commensurate with the objective of measurement and precisions of the measuring equipment and any quantities higher than that. In certain embodiments, the term "at least about" includes the recited number minus 10% and any quantity that is higher such that "at least about 10" would include 9 and anything greater than 9. This term can also be expressed as "about 10 or more." Similarly, the term "less than about" typically includes the recited number plus 10% and any quantity that is lower such that "less than about 10" would include 11 and anything less than 11. This term can also be expressed as "about 10 or less."

Unless otherwise indicated, all parts and percentages are by weight except that all parts and percentages of gas are by volume. Weight percent (wt %), if not otherwise indicated, is based on an entire composition free of any volatiles, that is, based on dry solids content. Volume percent (vol %), if not otherwise indicated, is based on the total volume of the gas.

Although the disclosure herein is with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the invention. It will be apparent to those skilled in the art that various modifications and variations can be made to the compositions and methods without departing from the spirit and scope of the invention. Thus, it is intended that the invention include modifications and variations that are within the scope of the appended claims and their equivalents.

Disclosed herein are methods of using a catalyst composition comprising zirconium oxide for dehydrogenation of light alkane gas (and/or light alkene gas) in the presence of hydrogen gas (H_2). Also disclosed are catalyst compositions, for example, that can be used in the dehydrogenation reaction, and methods of preparing such compositions. As a non-toxic, earth-abundant and low-cost oxide material, ZrO_2 (e.g., having a small crystallite size of less than about 10 nm, or less than about 20 nm, or less than about 30 nm, or less than about 50 nm, or less than about 1 μm) exhibits a high dehydrogenation rate (r_d) during propane dehydrogenation reactions. Pre-treating a standard ZrO_2 catalyst (e.g., precipitated using methods known to those of ordinary skill in the art) with carbon monoxide (CO) (e.g., for 30 min at 823 K) prior to use in a dehydrogenation reaction can result in a propane dehydrogenation rate of about 84 mol kg^{-1} h^{-1}, which is comparable to dehydrogenation rates exhibited with Pt-based materials. Without being bound to any particular theory, it may be that coordinatively unsaturated Zr sites (Zr_{cus}) are the active structures in ZrO_2 catalysts. With only a light alkane gas, such as propane (C_3H_8), in the inlet stream to a dehydrogenation process, the ZrO_2 catalyst may exhibit a half-life of only, for example, 0.2 h at 873 K, and rapid deactivation attributable to the formation of carbonaceous species on the surface of the ZrO_2. Regeneration of the ZrO_2 catalyst may require frequent cyclic operations based on dehydrogenation reactions and subsequent re-oxidation processes (e.g., in the operation of cycle Catofin-type processes). That is, while ZrO_2 catalysts exhibit favorable dehydrogenation activity during dehydrogenation reactions, they can suffer from rapid deactivation due to coke formation.

During investigations of light alkane gas dehydrogenation activity over a catalyst composition comprising ZrO_2 according to embodiments, it has been found that by co-feeding H_2 with the light alkane gas during the dehydrogenation reaction, the stability of the catalyst can be significantly increased. As set forth in the examples below, further studies have been conducted to verify this observation and to demonstrate the specific effect of H_2 on the activity of the catalyst composition comprising ZrO_2 during a light alkane dehydrogenation reaction while the bulk crystallite structure of the catalyst composition has been preserved during the reaction. According to various embodiments, the purposeful addition of H_2 to light alkane reactants during dehydrogenation reactions on catalyst compositions comprising ZrO_2 as the active material, leads to significant stability improvements, with half-life improvements of 100-fold upon addition of the H_2. Adding or co-feeding the H_2 with the light alkane gas can include introducing the H_2 at a pressure of about 1 kPa to about 100 kPa, or at a molar ratio of H_2 to light alkane gas of about 1:100 to about 1:1. In embodiments, the H_2 and/or reactor can be at a reaction temperature of about 500 K to about 1000 K, or about 873 K. The increase in stability may be attributed to the influence of H_2 on the formation of carbonaceous species.

To stabilize the catalyst composition comprising ZrO_2, hydrogen (H_2) (e.g., about 2-20 kPa) can be co-fed with the light alkane gas (and/or light alkene gas) during the dehydrogenation reaction. A significant increase in the stability of the catalyst composition comprising ZrO_2 can be achieved with more than a 100-fold increase in the catalyst's half-life. Without being bound by any particular theory, this increase in stability may be attributable to two factors: 1) the continuous regeneration of Zr active sites; and 2) the inhibition of coke formation via hydrogenative removal. As discussed above, the activity of catalyst compositions comprising ZrO_2 may be attributable to Zr surface-active sites on which light alkane molecules can be activated and dehydrogenated to alkenes or which could lead to the formation or organic species that themselves can act as a reaction-derived catalytic function on zirconia surfaces. A higher initial dehydrogenation rate also can be achieved through a pretreatment with a reducing gas (e.g., H_2, CO, NH_3, etc.) at a corresponding reaction temperature, possibly suggesting the generation of Zr surface-active sites as a result of the reductive pre-treatment. By co-feeding H_2 with the light alkane gas (and/or light alkene gas) during the dehydrogenation reaction, it may be that the Zr surface-active sites are continu-

ously regenerated so that loss of active sites due to coke formation are compensated for accordingly.

An inhibition effect on coke formation may be achieved by co-feeding H_2 with the light alkane gas (and/or light alkene gas) during dehydrogenation. Quantification of carbon dioxide (CO_2) generated during a reoxidation process demonstrates an 80% decrease in total coke amount during a propane dehydrogenation reaction in the presence of H_2 as will be discussed in more detail below with respect to FIG. **5**. Co-feeding H_2 with the light alkane gas (and/or light alkene gas) can maintain and/or increase the number of active sites in a catalyst composition comprising ZrO_2 and while simultaneously inhibiting coke formation, resulting in improved stability of catalyst compositions for light alkane gas (and/or light alkene gas) dehydrogenation reactions.

Without being bound by any particular theory, the continuous generation of Zr surface-active sites (e.g., Zr_{cus}) may be achieved as the H_2 removes lattice oxygen from the surface of the catalyst composition comprising ZrO_2. As discussed above, pretreating the catalyst compositions using a reducing gas (e.g., H_2, CO, NH_3, etc.) is believed to generate Zr surface-active sites and can result in a higher initial dehydrogenation rate (r_d). Nonetheless, it has been observed that a continuous decrease in dehydrogenation rate may still exist on reduced catalyst compositions comprising ZrO_2 during the dehydrogenation reaction without the presence of additional H_2 due to the formation of carbonaceous species. The formation of carbonaceous species on the catalyst surface under reaction conditions has been identified as a main cause of deactivation for most all dehydrogenation catalysts. These carbonaceous species can include hydrogen-poor organic residues that block active sites by hindering contact with reactants and removal of products. Without being bound by any particular theory, it may be that the addition of H_2 during the dehydrogenation reaction generates Zr active sites (e.g., Zr_{cus} active sites) by removing surface lattice oxygen, such that the lost active sites covered by carbonaceous species may be compensated during the dehydrogenation reaction; when all of the surface lattice oxygen is removed, this mechanism may change. In embodiments, the H_2 can be present in an amount sufficient to remove surface lattice oxygen from the catalyst composition and to generate and/or reactivate surface-active sites. For example, the H_2 can be present in an amount of H_2 per mass of catalyst of about 1 mol kg^{-1} h^{-1} to about 100 mol kg^{-1} h^{-1}, or about 55 mol kg^{-1} h^{-1}.

When comparing the amount of carbon dioxide (CO_2) generated during the re-oxidation process, a decrease (e.g., 80%) in the amount of carbonaceous species can be observed when H_2 (e.g., 12.3 kPa) is added to the light alkane inlet stream at, for example, a temperature of about 873 K. The decrease in the amount of carbonaceous species formed can be attributable to the inhibited adsorption of certain polymerization intermediates (e.g., C_2H_4, C_3H_6, etc.) as the catalyst surface is populated and present in equilibrium with the added H_2.

Catalyst Compositions

Catalyst compositions as described herein are useful in dehydrogenation reactions, for example, to dehydrogenate light alkane gases to form alkenes. In embodiments, the catalyst compositions can also be used to dehydrogenate light alkene gases to form alkadienes. According to embodiments, the catalyst compositions can comprise ZrO_2. The ZrO_2 is the active catalyst material in the dehydrogenation reactions according to various embodiments disclosed herein. In embodiments, the ZrO_2 is not inactive or an inactive support, rather it is the active catalyst material.

As will be discussed in more detail below, the catalyst composition may comprise an additive, such as yttrium, to increase the sintering stability and thus preserve the tetragonal phase of ZrO_2. The catalyst composition may also be free of at least one of chromium and a precious metal. Non-limiting examples of precious metals include platinum (Pt), gold (Au), silver (Ag), copper (Cu), palladium (Pd) and combinations thereof. In embodiments, the catalyst composition is free of both chromium and platinum. Catalyst compositions as described herein may present fewer risks to human health and the environment than other known catalysts, e.g., chromium- and platinum-based catalysts, used for dehydrogenation.

In embodiments, the catalyst composition can include at least about 50 wt % ZrO_2, at least about 60 wt % ZrO_2, at least about 70 wt % ZrO_2, at least about 80 wt % ZrO_2, at least about 90 wt % ZrO_2, or about 85 wt % ZrO_2, about 90 wt % ZrO_2, about 95 wt % ZrO_2, about 96 wt % ZrO_2, about 97 wt % ZrO_2, about 98 wt % ZrO_2, about 99 wt % ZrO_2, about 99.5 wt % ZrO_2, or about 100 wt % ZrO_2. In embodiments, the catalyst composition can include about 50 wt % to about 100 wt % ZrO_2, or about 60 wt % to about 100 wt % ZrO_2, or about 70 wt % to about 100 wt % ZrO_2, about 80 wt % to about 100 wt % ZrO_2, or about 90 wt % to about 100 wt % ZrO_2.

Catalyst compositions according to embodiments herein can contain a plurality of surface-active sites. Without being bound by any particular theory, for catalyst compositions comprising ZrO_2, it may be that the surface-active sites are coordinatively unsaturated Zr sites (Zr_{cus}). According to embodiments, catalyst compositions comprising ZrO_2 comprise a plurality of Zr_{cus} surface-active sites.

The catalyst compositions can be measured by X-ray diffraction (XRD), e.g., using a Siemens D5000 unit at ambient temperature with Cu Kα radiation and a scan rate of 0.033° s^{-1} to determine the crystalline structure of the catalyst composition. Catalyst compositions comprising ZrO_2 in embodiments disclosed herein can be in at least one of the monoclinic phase and the tetragonal phase, for example, as measured by XRD as described in Zhang, et al., *The Effect of Phase Composition and Crystallite Size on Activity and Selectivity of ZrO_2 in Non-Oxidative Propane Dehydrogenation*, J. of Catalysis, 371, 313-324 (2019), which is incorporated herein by reference in its entirety. In embodiments, the catalyst composition comprises ZrO_2 in the monoclinic phase.

The Brunauer, Emmett and Teller (BET) surface area of the catalyst composition can be measured using nitrogen (N_2) physisorption uptake at its normal boiling point in a surface analyzer (e.g., a Quantasorb® 6 Surface Analyzer by Quantachrome® Corp.). The BET surface area can be measured as set forth in Otroshchenko, et al., *Zr_2-Based Unconventional Catalysts for Non-Oxidative Propane Dehydrogenation: Factors Determining Catalytic Activity*, J. of Catalysis, 348, 282-290 (2017), which is incorporated herein by reference in its entirety. Another suitable method of measuring the BET surface area is set forth in ASTM D3663-03(2008), which is incorporated by reference herein in its entirety. Catalyst compositions comprising ZrO_2 as described herein can have a BET surface area of about 1 m^2 g^{-1} to about 100 m^2 g^{-1}, or about 10 m^2 g^{-1} to about 90 m^2 g^{-1}, or about 20 m^2 g^{-1} to about 80 m^2 g^{-1}, 30 m^2 g^{-1} to about 70 m^2 g^{-1}, 40 m^2 g^{-1} to about 60 m^2 g^{-1}, or about 40 m^2 g^{-1}, or about 45 m^2 g^{-1}, or about 50 m^2 g^{-1} as measured by a surface analyzer as described above.

According to various embodiments, the catalyst composition comprising ZrO_2 can further include a rare earth

metal. In embodiments, the rare earth metal can include at least one lanthanide metal, an oxide thereof and combinations thereof. According to embodiments, the rare earth metal can be at least one of yttrium (Y), erbium (Er), cerium (Ce), dysprosium (Dy), gadolinium (Gd), lanthanum (La), neodymium (Nd), samarium (Sm), ytterbium (Yb), oxides thereof and mixtures thereof. In embodiments, the catalyst composition can include about 0.5 wt % to about 50 wt %, or about 1 wt % to about 40 wt %, or about 2 wt % to about 30 wt %, or about 3 wt % to about 25 wt %, or about 4 wt % to about 20 wt %, or about 5 wt % to about 15 wt %, or about 1 wt % to about 12 wt %, or about 2 wt % to about 10 wt % of the rare earth metal, an oxide thereof or mixtures thereof. In certain embodiments, the catalyst composition can include ZrO_2 stabilized with an yttrium dopant. The yttrium can increase the surface area of ZrO_2 and stabilizes the pure tetragonal phase of the ZrO_2. Such catalyst compositions can comprise about 85 wt % to about 99.5 wt % ZrO_2 and about 0.5 wt % to about 15 wt % Y_2O_3 and/or anatomic ratio of Y/Zr of greater than 0 to about 0.2. The catalyst composition comprising the yttria-stabilized zirconia (YSZ) can have a BET surface area of about 40 $m^2 g^{-1}$ to about 110 $m^2 g^{-1}$.

According to various embodiments, a catalyst composition comprising ZrO_2 can be treated with a pretreatment gas. Pretreating the catalyst composition can increase the number of surface-active sites on the catalyst, which can result in higher catalytic activity during the dehydrogenation reaction (e.g., at the beginning of the reaction). For example, without being bound by any particular theory, it may be that pretreating a catalyst composition comprising ZrO_2 can increase the Zr surface-active sites as compared to a catalyst composition that has not been pretreated. In embodiments, a pretreated catalyst composition containing ZrO_2 comprises more surface-active sites (e.g., Zr_{cus}) than a catalyst composition containing ZrO_2 that has not been pretreated.

In embodiments, a pretreated catalyst composition can be formed by contacting the catalyst composition with a pretreatment gas under certain conditions. The pretreatment gas can include a reducing agent comprising at least one of H_2, carbon monoxide (CO), ammonia and methane (CH_4). In embodiments, the pretreatment gas can further include an inert gas comprising at least one of nitrogen (N_2), helium (He) and Argon (Ar). In embodiments, the pretreatment gas can comprise the reducing agent at a concentration of about 1 mol % to about 10 mol %, or about 2 mol %, or about 4 mol %, or about 6 mol %, or about 8 mol %, or about 10 mol %. In certain embodiments, the pretreatment gas is H_2 and can include about 1 mol % to about 10 mol % H_2, or about 2 mol % H_2, or about 4 mol % H_2, or about 6 mol % H_2, or about 8 mol % H_2, or about 10 mol % H_2.

During the pretreatment, the pretreatment gas and/or the catalyst composition can be at a temperature of at least about 850 K, or at least about 860 K, or at least about 870 K, or at least about 873 K, or at least about 880 K, or at about 870 K, or at about 871 K, or at about 872 K, or at about 873 K, or at about 874 K, or at about 875 K. The pretreatment gas can be in contact with the catalyst composition for about 1 h to about 24 h, or about 2 h to about 22 h, or about 3 h to about 20 h, or about 5 h to about 15 h, or about 8 h to about 12 h, or about 1 h, or about 2 h, or about 3 h, or about 4, hour or about 5 h.

According to various embodiments, catalyst compositions as disclosed herein can be in the form of a plurality of units. The plurality of units can include, but are not limited to, particles, powder, extrudates, tablets, pellets, agglomerates, granules and combinations thereof. The plurality of units can have any suitable shape known to those of ordinary skill in the art. Non-limiting examples of shapes include round, spherical, spheres, ellipsoidal, cylinders, hollow cylinders, four-hole cylinders, wagon wheels, regular granules, irregular granules, multilobes, trilobes, quadrilobes, rings, monoliths and combinations thereof.

The plurality of units can be formed by any suitable method known to those of ordinary skill in the art. Non-limiting examples of methods for shaping and forming a plurality of units (e.g., from a mixture of catalyst materials) include, extrusion, spray drying, pelletization, agglomeration, oil drop, and combinations thereof. In one embodiment, the plurality of units can be formed by pressing a powder into wafers (e.g., at about 690 bar, for about 0.05 h), crushing the wafers and then sieving the resulting aggregates to retain a mean aggregate size of about 100 μm to about 250 μm, or about 1.5 mm to about 5 mm, or about 80 mesh to about 140 mesh.

In certain embodiments, the plurality of units can have a size of less than about 1,000 μm, or less than about 750 μm, or less than about 500 μm, or less than about 300 μm, or less than about 250 μm, or less than about 225 μm, or less than about 200 μm, or less than about 190 μm, or less than about 180 μm, or less than about 150 μm, or less than about 100 μm, or less than about 10 μm as measured by any suitable method known to those of ordinary skill in the art. In embodiments, the plurality of units can have a size of about 170 μm to about 250 μm, or about 80 mesh to about 140 mesh. In further embodiments, the plurality of units have a mean size of about 1.5 mm to about 15.0 mm, or about 1.5 mm to about 12 mm, or about 1.5 mm to about 10 mm, or about 1.5 mm to about 8.0 mm, or about 1.5 mm to about 5.0 mm. Particle size can be measured using any suitable method known to those of ordinary skill in the art. For example, particle size can be measured using ASTM D4438-85(2007) and ASTM D4464-10, both of which are incorporated herein by reference in their entirety.

According to embodiments, catalyst compositions as described herein may be comprised in a kit. The kit can include the catalyst composition as described above and instructions for pretreating the catalyst composition. The instructions can comprise the following elements: 1) place the catalyst composition in a chamber and/or reactor; 2) heat the pretreatment gas, the chamber, the reactor and/or the catalyst composition to a temperature of at least about 850 K, or at least about 860 K, or at least about 870 K, or at least about 873 K, or at least about 880 K. or at about 870 K, or at about 871 K, or at about 872 K, or at about 873 K, or at about 874 K, or at about 875 K; 3) introduce the pretreatment gas into the chamber and/or reactor and contact the catalyst composition with the pretreatment gas for about 0.1 h to about 24 h, or about 0.5 h to about 22 h, or about 1.0 h to about 20 h, or about 2.5 h to about 15 h, or about 5 h to about 12 h, or about 0.1 h, or about 0.2 h, or about 0.5 h, about 1 h, or about 2 h, or about 3 h, or about 4, hour or about 5 h.

According to embodiments, the kit may include the catalyst composition together with instructions for using the catalyst composition in a light alkane (or light alkene) dehydrogenation process. The catalyst composition can be pretreated or may not be pretreated in accordance with embodiments herein. If not pretreated, the kit can further include instructions for pretreating the catalyst composition as described above. The instructions for using the catalyst composition can comprise the following elements: 1) place the catalyst composition in a reactor; 2) introduce the light alkane gas (and/or light alkene gas) together with H_2 into the

reactor; and 3) contact the light alkane gas (and/or light alkene gas) and the H_2 with the catalyst composition. Optionally, the instructions may further include 4) recover the dehydrogenated (i.e., alkene or alkadiene) gas.

The kits discussed above can include suitable details and instructions for using the catalyst composition safely and productively. Non-limiting examples of such details and instructions can include how to load the catalyst composition into the reactor, how to pre-treat the catalyst composition, if necessary, before starting the reaction, the starting temperatures and gas composition for bringing the catalyst composition on-stream, the regeneration procedures, how to unload the catalyst composition from the reactor and combinations thereof.

Methods of Preparing the Catalyst Compositions

According to various embodiments, disclosed herein are methods of preparing catalyst compositions as described above. A catalyst composition comprising ZrO_2 can be prepared using a hydrothermal approach. In embodiments, the catalyst composition comprising ZrO_2 can be synthesized by dissolving an amount of $ZrO(NO_3)_2xH_2O$ in an amount of water (e.g., deionized water) at a weight ratio of water to $ZrO(NO_3)_2xH_2O$ of about 1:1 to about 5:1, or about 2:1 to about 4:1, or about 2:1, or about 2.3:1, or about 2.4:1, or about 3:1, or about 4:1. Separately urea can be dissolved in water at a weight ratio of water to urea of about 1:2 to about 4:1, or about 1:1 to about 3:1, or about 1.5:1 to about 2:1, or about 1.1:1, or about 1.2:1, or about 1.3:1, or about 1.4:1. The $ZrO(NO_3)_2xH_2O$ and urea solutions can be mixed together at a temperature of about 20° C. to about 25° C. and then transferred to an autoclave formed of a suitable material (e.g., stainless steel or other metallurgy, Teflon® or other suitable polymer). The mixture can be crystallized in the autoclave at an elevated temperature, for example, a temperature of about 300 K to about 500 K, or about 320 K to about 480 K, or about 350 K to about 460 K, or about 400 K, or about 450 K, or about 451 K, or about 452 K, or about 453 K, or about 454 K, or about 455 K under autogenous pressure for a period of time, for example, about 2 h to about 36 h, or about 5 h to about 32 h, or about 10 h to about 24 h, or about 12 h to about 20 h, or about 18 h, or about 19 h, or about 20 h, or about 21 h, or about 22 h. The crystalline precipitate can be washed with deionized water, for example, at a ratio of about 50 mL to about 250 mL of deionized water per gram of catalyst, or about 100 mL deionized water per g catalyst and subsequently dried under air at a temperature of about 300 K to about 500 K, or about 325 K to about 450 K, or about 350 K to about 400 K, or about 380 K, or about 381 K, or about 382 K, or about 383 K, or about 384 K, or about 385 K, for a period of about 6 h to about 24 h, or about 8 h to about 22 h, or about 10 h to about 20 h, or about 12 h to about 18 h. In embodiments, the crystalline precipitate can be calcined according to any suitable method known to those of ordinary skill in the art. For example, the crystalline precipitate can be calcined in flowing dry air (e.g., zero grade) at a flow rate of about 0.5 $cm^3\ s^{-1}$ to about 2.00 $cm^3\ s^{-1}$, or about 1.67 $cm^3\ s^{-1}$ and a temperature of about 700 K to about 1,000 K, or about 750 K to about 950 K, or about 800 K to about 900 K, or about 870 K, or about 871 K, or about 872 K, or about 873 K, or about 874 K, or about 875 K, or about 923 K, for about 1 h to about 6 h, or about 3 h.

In embodiments, a catalyst composition comprising yttrium stabilized zirconium oxide can be prepared. The catalyst composition can be synthesized by combining $ZrO(NO_3)_2$ with $Y(NO_3)_3$, NH_4OH and H_2O to form a mixture. The mixture can be transferred to an autoclave to be crystallized at an elevated temperature of about 250 K to about 500 K, or about 275 K to about 480 K, or about 290 K to about 460 K, or about 295 K, or about 296 K, or about 297 K, or about 298 K, or about 299 K, or about 300 K, or about 301 K under autogenous pressure for a period of time, for example, about 2 h to about 36 h, or about 5 h to about 32 h, or about 10 h to about 24 h, or about 12 h to about 20 h, or about 10 h, or about 11 h, or about 12 h, or about 13 h, or about 14 h. The crystalline precipitate can be washed with deionized water, for example, at a ratio of about 50 mL to about 250 mL of deionized water per gram of catalyst, or about 100 mL deionized water per g catalyst, and subsequently dried under air at a temperature of about 300 K to about 500 K. or about 325 K to about 450 K, or about 350 K to about 400 K, or about 380 K, or about 381 K, or about 382 K. or about 383 K, or about 384 K, or about 385 K, for a period of about 6 h to about 24 h, or about 8 h to about 22 h, or about 10 h to about 20 h, or about 12 h to about 18 h. In embodiments, the crystalline precipitate can be calcined according to any suitable method known to those of ordinary skill in the art. For example, the crystalline precipitate can be calcined in flowing dry air (e.g., zero grade) at a flow rate of about 0.5 $cm^3\ s^{-1}$ to about 2.00 $cm^3\ s^{-1}$, or about 1.67 $cm^3\ s^{-1}$ and a temperature of about 700 K to about 1.000 K, or about 750 K to about 950 K, or about 800 K to about 900 K, or about 870 K, or about 871 K, or about 872 K, or about 873 K, or about 874 K, or about 875 K, or about 923 K, for about 1 h to about 6 h, or about 3 h.

According to embodiments, methods of preparing the catalyst composition can further include pretreating the catalyst composition in a pretreatment gas as discussed above. For example, the catalyst composition can be subjected to a reductive pretreatment, for example, with a pretreatment gas comprising at least one of H_2, carbon monoxide (CO), light alkanes, propane (C_3H_8), alkenes, propene (C_3H_6) and H_2 species present as reactant and products of the dehydrogenation reaction. In embodiments, the catalyst composition can be pretreated with H_2 at a temperature of about 800 K to about 1,000 K, or about 850 K to about 900 K, or about 873 K. The pretreated catalyst composition can include more surface-active sites (e.g., Zr_{cus} surface-active sites) than a catalyst composition that has not been pretreated.

Methods of Using the Catalyst Compositions

Further described are methods of using catalyst compositions according to embodiments. In embodiments, the catalyst compositions can be used in the dehydrogenation of light alkane gas to form alkenes. In embodiments, the methods can also be used in the dehydrogenation of light alkene gas to form alkadienes. The ZrO_2 present in the catalyst compositions is the active catalyst material in the dehydrogenation reactions as disclosed herein. In contrast to, e.g., the Oleflex® process where ZrO_2 is used as an inactive support for the active Pt—Sn catalyst materials, the ZrO_2 in the present catalyst compositions is the active catalyst material. It is believed that ZrO_2 has not before been used as the active catalyst material for the dehydrogenation of light alkane (and/or light alkene) gas according to embodiments herein.

In embodiments, when preparing to dehydrogenate a light alkane gas, the catalyst composition (e.g., at a weight hourly space velocity of about 5.5 h^{-1} to about 0.05 h^{-1}, or about 5.4 h^{-1} to about 0.054 h^{-1}, or about 2.7 h^{-1} to about 1.8 h^{-1}, or about 5.0 h^{-1} to about 0.1 h^{-1}) can be placed within a reactor and held at an about constant temperature using a furnace and a temperature controller (e.g., a Watlow Series 96). The reactor can be any suitable reactor known to those

of ordinary skill in the art. Non-limiting examples include a U-shape quartz reactor (e.g., with an inner diameter of about 11.0 mm), a packed tubular reactor, a catofin-type reactor, a fluidized bed reactor, a fixed bed reactor and a moving bed reactor. The furnace may be any suitable furnace known to those of ordinary skill in the art. Non-limiting examples include a single zone furnace (e.g., by National Element Inc., Model No. BA-120), a batchwise furnace or a quartz tube furnace.

Prior to dehydrogenation, the catalyst composition can be treated in a flowing oxygen gas (O_2) and helium (He) mixture at a molar ratio of 02 of 20:1 to about 30:1, or about 22:1 to about 28:1, or about 24:1 and heating the flowing gas mixture to a temperature of about 800 K to about 1,000 K, or about 850 K to about 900 K, or about 873 K at a rate of about 0.1 K s' to about 1 K s^{-1}, or about 0.167 K s^{-1}. Treating the catalyst composition with the flowing O_2 and He gas mixture can be for a period of about 0.5 h to about 8 h, or about 1 h to about 4 h, or about 1 h, or about 2 h. Subsequently, the reactor can be purged with flowing inert gas (as defined above), steam, or by vacuum (e.g., 2 cm^3 g^{-1} s^{-1}, ultra-high purity) to remove residual O_2 within the reactor.

The light alkane gas (and/or light alkene gas) can be introduced to the reactor in the presence of the catalyst composition. According to embodiments, the light alkane gas (and/or light alkene gas) can comprise any one of a C_2 to C_5 straight or branched alkane and mixtures thereof. In embodiments, the light alkane gas (and/or light alkene gas) can comprise at least one of ethane, propane, n-butane, isobutane, pentane and mixtures thereof. In embodiments, a portion of the effluent from the reactor can be recycled to the gas inlet and combined with fresh feed gas. The effluent can comprise alkenes, for example, at least one of ethene, pentene, butene, isobutene and pentene, and unreacted light alkanes comprising at least one of ethane, propane, n-butane, isobutane and pentane. In embodiments, the light alkane gas (and/or light alkene gas) can be mixed with an inert gas (e.g., steam, He, N_2, Ar) at a molar ratio of about 1:2 to about 2:1, or about 1:1. In embodiments, a vacuum pump can be used to lower the pressure of the reactants while maintaining the total pressure above, for example, 1 bar to allow convective flow when the exit pressure is atmospheric.

Methods of dehydrogenating light alkane gas (and/or light alkene gas) can include co-feeding H_2 with the light alkane gas (and/or light alkene gas) in the presence of the catalyst composition. The catalyst composition can comprise ZrO_2 according to various embodiments described herein. Adding or co-feeding the H_2 with the light alkane gas (and/or light alkene gas) can include introducing the H_2 at a pressure of about 1 kPa to about 100 kPa, or about 5 kPa to about 75 kPa, or about 10 kPa to about 50 kPa, or about 30 kPa to about 50 kPa while dehydrogenating the light alkane gas. In embodiments, the H_2 can be added to the light alkane gas (and/or light alkene gas) at a molar ratio of H_2 to light alkane gas (and/or light alkene gas) of about 1:100 to about 1:1. In embodiments, the H_2 and/or reactor can be at a temperature of about 500 K to about 1000 K, or about 550 K to about 950 K, or about 600 K to about 900 K, or about 700 K to about 900 K.

According to embodiments, the method of dehydrogenating a light alkane gas (and/or light alkene gas) in the presence of H_2 and a catalyst composition as described herein can provide a dehydrogenation rate per mass of the catalyst composition of about 0.5 mol kg^{-1} h^{-1} to about 10.0 mol kg^{-1} h^{-1}, or about 0.6 mol kg^{-1} h^{-1} to about 8.3 mol kg^{-1} h^{-1}. The light alkane gas (and/or light alkene gas) dehydrogenation rate and cracking rate can be determined by analyzing the effluent stream from the reactor using gas chromatography (e.g., by an Agilent® 1540A gas chromatograph) with flame ionization detection (FID) (e.g., a GC fitted with a GS-GASPRO column) after chromatographic separation. In embodiments, the light alkane gas (and/or light alkene gas) dehydrogenation rate and the cracking rate can be normalized by the mass of the catalyst composition (e.g., in mol kg^{-1} h^{-1}). In embodiments, the light alkane gas (and/or light alkene gas) dehydrogenation rate and cracking rate can be determined at a temperature of 873 K and 823 K. The temperature can be measured using any suitable method known to those of ordinary skill in the art. In embodiments, the temperature can be measured with a thermocouple (e.g., a K-type thermocouple by Omega®) and the reactor temperature can be determined from a thermocouple placed in contact with an outer tube surface (e.g., made of metal, quartz, etc.) at the catalyst bed midpoint.

In embodiments, when used in a dehydrogenation reaction as described above, catalyst compositions as disclosed herein can provide improved stability over other known catalyst compositions for the dehydrogenation of light alkanes (and/or light alkenes). The half-life of the catalyst composition in the dehydrogenation reaction can be measured using any suitable method known to those of ordinary skill in the art. In embodiments, the term "half-life of the catalyst composition" can refer to the number of days or hours after which the catalyst device has a dehydrogenation rate (DR) that is 50% lower than an initial or maximum dehydrogenation rate (DR_i) value produced by the catalyst composition at the start (or soon after the start upon stabilization) of the catalyst composition's operation (e.g., the half-life of the catalyst composition can be based on the dehydrogenation reaction rate as a function of time). In embodiments, the half-life of the catalyst composition is related to the weight hourly space velocity (WHSV), which is the hourly mass feed flow rate per catalyst mass (h^{-1}) in the reactor. In embodiments, the catalyst composition can have a half-life of about 1 h to about 50 h, or about 6 h to about 46 h when the WHSV is about 5.4 h^{-1} to about 0.054 h^{-1}.

The half-life of the catalyst composition can also be evaluated when aging the composition under different conditions. The DR can be calculated based on Formula I:

$$DR=60\cdot(k_e-k_n)\cdot V \qquad \text{Formula I}$$

wherein k_e represents the total decay constant, k represents natural decay constant, V represents the chamber volume in m^3, and (k_e-k_n) is calculated based on Formula II:

$$(k_e-k_n)\cdot t=-\ln(C_t/C_0) \qquad \text{Formula II}$$

wherein t represents the total testing time, C_t represents the concentration at time t in mg/m^3, and C_0 represents the concentration at time t=0 in mg/m^3.

To determine the half-life of the catalyst composition, testing can begin by obtaining the DR value produced by the catalyst composition at the start of the catalyst composition's operation or soon after the start of the catalyst composition's operation once the DR has stabilized (t=0), also known as DR_0. Subsequently, the catalyst composition can be optionally subjected to an Acceleration Test. An "Acceleration Test" refers to an extreme condition that may impact or deteriorate the efficacy of the catalyst composition more rapidly, such as no H_2 gas co-feed or pre-treatment, co-feeding with O_2, introducing a pollutant or continuous generation of pollutants. The optional Acceleration Test

results can allow the estimation of the catalyst composition's life span under real-life conditions. Following the optional Acceleration Test, the catalyst composition is then aged under real-life conditions.

After the catalyst composition is aged for eight hours under real-life conditions, another sample is taken to obtain the DR_n value at t=n, also known as DR_n. If the DR_n value is greater than 50 percent of the DR_n value, then the catalyst composition is considered as still operable and the testing continues by repeating the optional acceleration test, aging the catalyst device under real-life conditions, and measuring the DR_n value after each subsequent cycle. Once the DR_n value is lower or equal to 50 percent of the DR_0 value, the life span of the catalyst device is deemed to have ended and the overall alkene mass (AM) generated by the catalyst composition is calculated.

The above-described methods of using the catalyst compositions to dehydrogenate light alkane gas, can also be used to dehydrogenate a light alkene gas to form alkadienes. A light alkene gas can include C_2-C_5 branched or straight alkenes. In embodiments, two reactors can be configured in series, the first for dehydrogenating light alkane gas and the second for dehydrogenating the light alkene gas.

EXAMPLES

Example 1—Crystal Structure of ZrO_2

A ZrO_2 catalyst composition was prepared using a hydrothermal approach. To synthesize the ZrO_2, 12.7 g $ZrO(NO_3)$ $2xH_2O$ (99%, Aldrich) were dissolved in 30 mL deionized H_2O and 21.6 g urea were dissolved in 30 mL deionized H_2O separately. The resulting solutions were mixed together at room temperature and then transferred into a Teflon lined stainless-steel autoclave. Crystallization was performed at 453 K under autogenous pressure for 20 h. After completion of the crystallization process, the precipitate was washed thoroughly with 500 ml deionized water and then dried under air at 383 K overnight.

The crystal structure of the resulting ZrO_2 catalyst composition was measured using X-ray diffraction. The XRD pattern of ZrO_2 catalyst composition is shown in FIG. **1**. The data herein indicates that catalyst compositions as described can retain the tetragonal phase at all temperatures of treatment while providing higher dehydrogenation rates.

Example 2—Effect of Pretreatment on Initial C_3H_8 Dehydrogenation Rate (r_d) at 873 K

The effect of pretreating the ZrO_2 catalyst composition as prepared in Example 1 on initial propane dehydrogenation (PDH) rate (r_d) at 873 K was evaluated. In order to compare the effect of oxidative and reductive pretreatments on PDH activity of the ZrO_2 catalyst composition, the catalyst was pretreated in a 4 mol % O_2/He mixture at 873 K for 2 h and separately in a 10 mol % H_2/He mixture at 873 K for 2 h prior to the PDH reaction.

The O_2/He pretreated ZrO_2 catalyst was introduced into the reactor. During the propane dehydrogenation reaction, the propane feed gas was at a pressure of 13.7 kPa and a temperature of 873 K and the catalyst composition was at a temperature of 873 K. As shown in FIG. **2**A, an initial increase in dehydrogenation rate (per mass) was observed within 6 min of the reaction. The dehydrogenation rate increased from 5.2 mol kg^{-1} h^{-1} to 7.8 mol kg^{-1} h^{-1} while the selectivity of the PDH reaction (ratio between dehydrogenation and cracking rate (r_d/r_c)) also increased from 71 to 88 during this 6 min activation period. A monotonic decrease in dehydrogenation rate and selectivity was observed after the initial activation period indicating the deactivation of ZrO_2 catalyst. Without being bound by any particular theory, the increase in dehydrogenation rate during the initial activation period may indicate the presence of an activation effect. Because the surface lattice oxygen was removed, Zr surface active sites possibly were generated leading to a higher dehydrogenation rate.

After the initial activation period of 6 min, the dehydrogenation rate and selectivity (r_d/r_c) of ZrO_2 catalyst decreased with time. The deactivation process follows a first-order deactivation mechanism as shown in equation 1:

$$\ln\left(\frac{r_i}{r_0}\right) = -k_d t \tag{1}$$

where r_0 is the maximum dehydrogenation rate at the beginning of PDH reaction or during the initial activation period, r_i is the dehydrogenation rate at different time on stream and k_d is the deactivation constant. The half-life of the catalyst is defined in equation 2, which is time elapsed as the catalyst deactivates to one-half of its initial dehydrogenation rate:

$$t_{0.5} = \left|\frac{\ln(0.5)}{k_d}\right| \tag{2}$$

FIG. **2**A shows that after the initial activation period during PDH reaction at 873 K, a half-life of 0.28 h can be observed for the ZrO_2 catalyst pretreated in O_2/He at 873 K and the deactivation is mainly caused by the formation of carbonaceous species on the surface, as the spent catalyst exhibited black color. This observation confirms previous observations (see, e.g., Zhang, et al., *Control of Coordinatively Unsaturated Zr Sites in ZrO_2 for Efficient C-H Bond Activation*, Nature Communications, 9 (1), 3794 (2018)) that ZrO_2 catalysts during PDH reaction suffer from rapid deactivation with a catalyst's half-life of 0.2 h during PDH reaction at 873 K under 40 kPa C_3H_8 and require regeneration on a regular basis.

A fresh catalyst was treated in flowing 10% H_2/He mixture at 873 K for 2 h. As shown in FIG. **2**B, for the ZrO_2 catalyst pretreated in the H_2/He, the initial activation period was not observed during the PDH reaction at 873 K. The initial dehydrogenation rate was 8.3 mol kg^{-1} h^{-1}, which is comparable to the highest dehydrogenation (i.e., 7.8 mol kg^{-1} h^{-1}) during initial activation period on ZrO_2 treated in 4% O_2/He at 873 K. This indicates that a reductive pretreatment by H_2 can activate ZrO_2 to a similar extent as an oxidative pretreatment during the initial activation period. The dehydrogenation rate on ZrO_2 treated in H_2/He at 873 K decreased monotonically with time on stream with a half-life of 0.32 h, a value similar to that on ZrO_2 treated in O_2/He at 873 K (0.28 h). This indicates that the deactivation behavior is not affected by pretreatment methods (oxidative or reductive). Based on the above observation, it was determined that H_2 can activate the ZrO_2 catalyst through H_2/He pretreatment before the PDH reaction.

Example 3—Dehydrogenation Rate Per Mass of Catalyst (r_d) During a C_3H_8 Dehydrogenation Reaction on a Pretreated ZrO_2 Catalyst

The dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction on a pretreated ZrO_2 catalyst was deter-

mined. A ZrO_2 catalyst composition as prepared in Example 1 was pretreated with O_2 at a pressure of 4 kPa and a temperature of 823 K for 2 h. Separately, another ZrO_2 catalyst composition as prepared in Example 1 was pretreated in H_2 at a pressure of 10 kPa and a temperature of 873 K for 2 h. The effect of pretreatment was then studied for a PDH reaction at 823 K on the ZrO_2 catalyst During the PDH reaction, propane was introduced to the reactor at a pressure of 13.7 kPa and a temperature of 823 K.

As shown in FIG. **3**, after the catalyst was treated in O_2/He at 823 K, an initial activation effect was observed, which lasted for 70 min with an increase in dehydrogenation rate from 0.6 mol kg^{-1} h^{-1} to 0.7 mol kg^{-1} h^{-1}. After the initial activation period, the catalyst started to deactivate at a much slower rate as compared to the deactivation process during the PDH reaction at 873 K (Example 2). Moreover, for the PDH reaction at 823 K, there is no contribution to cracking rate from the ZrO_2 catalyst and all cracking products detected can be attributed to homogenous gas phase reactions of propane, which can occur even in empty reactors at these temperatures. The half-life for the catalyst pretreated with O_2/He during PDH reaction at 823 K was 34 h, which is 120 times higher than the half-life during the PDH reaction at 873 K (0.28 h). The ZrO_2 catalyst treated in H_2/He at 873 K had a higher initial dehydrogenation rate (1.1 mol kg^{-1} h^{-1}) compared with the catalyst (0.7 mol kg^{-1} h^{-1}) treated in O_2/He at 823 K during PDH reaction at 823 K. These data demonstrate the activation effect of the H_2 pretreatment (FIG. **3**).

Different from the PDH reaction at 873 K on the ZrO_2 catalyst treated in H_2/He at 873 K where no initial activation period can be observed, the PDH reaction at 823 K on the ZrO_2 catalyst treated in H_2/He at 873 K exhibited an initial activation period (110 min, up to 1.8 mol kg^{-1} h^{-1}). This indicates that the pre-reduced ZrO_2 can be further activated during the PDH reaction by propane-derived species. A 6 h half-life can be observed for ZrO_2 treated in H_2/He at 873 K during PDH reaction at 823 K, as compared to the ZrO_2 catalyst treated in O_2/He at 823 K (34 h).

Example 4—Effect of Co-Feeding H_2 on the Stability of ZrO_2 Catalyst at 873 K and 823 K

The effect of co-feeding H_2 with the light alkane gas (e.g., propane) during a dehydrogenation reaction in the presence of a ZrO_2 catalyst (as prepared in Example 1) was evaluated. The dehydrogenation rate per mass (r_d) of ZrO_2 catalyst pretreated with O_2/He, with additional H_2 present during the PDH reaction at different temperatures, was determined. During the PDH reaction, H_2 was introduced to the reactor at a pressure of 12.3 kPa and C_3H_8 was co-introduced at a pressure of 13.7 kPa. The reaction was performed at a temperature of 873 K and separately at a temperature 823 K.

Prior to the PDH reaction, the catalyst was pretreated in O_2/He at corresponding temperatures corresponding the PDH reaction temperatures (i.e., 823 K, 873 K). As the H_2 was co-fed into the reaction gas stream comprising C_3H_8, an inhibition effect on dehydrogenation rate was observed at 823 K. As shown in FIG. **4**, the initial dehydrogenation rate at 823 K decreased from 0.7 mol kg^{-1} h^{-1} to 0.31 mol kg^{-1} h^{-1}. Also shown in FIG. **4**, the initial dehydrogenation rate at 873 K decreased from 5.2 mol kg^{-1} h^{-1} to 2.5 mol kg^{-1} h^{-1}.

It was also found that there was no contribution to the cracking rate from the ZrO_2 catalyst during the PDH reaction with the additional H_2 at a pressure of 12.3 kPa at temperatures of 823 K and 873 K. The lack of contribution to the cracking rate at 873 K indicates that co-feeding with H_2 can improve the selectivity of the ZrO_2 catalyst towards C_3H_8.

The stability of the ZrO_2 catalyst improved in the PDH reaction when additional H_2 was co-fed with the propane at a pressure of 12.3 kPa and a temperature of 873 K. Indeed, the catalyst half-life was 46 h as compared to 0.28 h during the PDH reaction at 873 K without co-feeding with H_2. At 823 K, there was no observable deactivation during the PDH reaction under the presence of additional H_2 at a pressure of 12.3 kPa. Because H_2 pretreatment can activate the catalyst as demonstrated in Example 3, it is possible that by co-feeding H_2 during the PDH reaction, Zr_{cus} surface-active sites may be generated or maintained continuously so that any formation of carbonaceous species does not affect the catalytic activity.

FIG. **5** shows the CO_2 generation rate during a re-oxidation process after a PDH reaction with and without the presence of additional H_2 at 873 K on the ZrO_2 catalyst. During the re-oxidation, a mixture of 4% O_2/He was provided at a rate of 2 cm^3 g^{-1} s^{-1} and a temperature of 873 K. By comparing the total amount of CO_2 generated during the re-oxidation process, it was found that by co-feeding the H_2 with the propane feed gas, the formation of carbonaceous species could be inhibited.

After the PDH reaction at 873 K on the ZrO_2 catalyst pretreated with O_2/He, the total amount of CO_2 generated during the subsequent re-oxidation process was 2.6 mmol g_{cat}^{-1}, which corresponds to a surface carbon density of 35 C-atoms/nm^2. Considering the surface Zr—O pair density of 7 nm^{-2}, the formation of carbonaceous species is likely to cover the active sites on ZrO_2 catalyst surface, which can eventually lead to deactivation. After the PDH reaction with additional 12.3 kPa H_2 at 873 K on ZrO_2 catalyst with O_2/He pretreatment, only 0.5 mmol g_{cat}^{-1} CO_2 was generated during subsequent re-oxidation process, which corresponds to a surface carbon density of 6.6 nm^{-2} (FIG. **5**). The presence of additional H_2 at a pressure of 12.3 kPa during the PDH reaction at 873 K, led to a greater than five-fold decrease in the surface density of carbonaceous species as compared to the PDH reaction at 873 K without additional H_2. Together with the observed activation effect on the ZrO_2 catalyst during the PDH reaction after H_2 pretreatment, the stabilization of ZrO_2 during the PDH reaction by co-feeding H_2 may be attributable to continuous generation of surface-active sites while the formation of carbonaceous species is effectively inhibited. Without being bound by any particular theory, these data seem to indicate that the role of H_2 is to continuously remove the C as it forms at a rate higher than that achieved by the H_2 formed in situ by the dehydrogenation reaction. These two effects of pre-treatment and co-feeding with H_2 lead to a stable ZrO_2 catalyst during the PDH reaction with high selectivity towards propene.

Examide 5—Dependence of Dehydrogenation Rate on H_2 and C_3H_8

The dependence of the dehydrogenation rate on H_2 and C_3H_8 was evaluated. The dehydrogenation rate per mass of catalyst (r_d) was determined during a PDH reaction with additional H_2 at a pressure of 12.3 kPa and a temperature of 873 K on the ZrO_2 catalyst as a function of C_3Ha partial pressure. Due to the stabilization effect on the activity of the ZrO_2 catalyst during the PDH reaction with additional H_2, the dependence of the dehydrogenation rate on the partial pressure of C_3H_8 could be accurately determined at 873 K under the presence of additional H_2 at a pressure of 12.3 kPa

for a ZrO_2 catalyst pretreated in O_2/He at 873 K. As shown in FIG. **6**, the dehydrogenation rate increased proportionally with increasing C_3H_8 partial pressure while there was no contribution to cracking rate from the ZrO_2. This trend indicates that at 873 K the PDH reaction occurs on the surface with low coverages of C_3H_8-derived species, which are either weakly-bound or scavenged in fast subsequent reactions after they formed.

FIG. **7**A shows the dehydrogenation rate per mass of catalyst (r_d) during a PDH reaction where the propane gas was co-fed with H_2 at a pressure of 12.3 kPa or 24.6 kPa and a temperature of 823 K on the ZrO_2 catalyst as a function of C_3H_8 partial pressure. FIG. **7**B shows the dehydrogenation rate per mass of catalyst (r_d) during the PDH reaction where the propane gas was introduced at a pressure of 4.1 kPa, 13.7 kPa and 30.1 kPa and a temperature of 823 K on the ZrO_2 catalyst as a function of H_2 partial pressure.

The dependence of dehydrogenation rate on C_3H_8 and H_2 partial pressure at 823 K was determined for a ZrO_2 catalyst pretreated in O_2/He at 823 K. Under 12.3 kPa of additional H_2, an inhibition of dehydrogenation rate at elevating C_3H_8 partial pressure was observed at 823 K. This indicates that under additional H_2 at a pressure of 12.3 kPa, the catalyst surface has become saturated with C_3H_8-derived intermediates at high C_3H_8 partial pressure (FIG. **7**A), which can inhibit the dehydrogenation rate.

As the partial pressure of additional H_2 increased to 24.6 kPa, the dehydrogenation rate increased proportionally with increasing C_3H_8 partial pressure at 823 K, indicating that under additional H_2 at a pressure of 24.6 kPa, the C_3H_8-derived intermediates can undergo fast subsequent reaction on the catalyst surface and the dehydrogenation rate will not be inhibited. No contribution to cracking rate from the ZrO_2 was observed during the above mentioned PDH reaction under 12.3 kPa and 24.6 kPa of additional H_2.

As shown in FIG. **7**B, the dependence of dehydrogenation rate on H_2 partial pressure was studied under 4.1 kPa, 13.7 kPa and 30.1 kPa C_3H_8 at 823 K. An inhibition effect on the dehydrogenation rate was observed for all three C_3H_8 partial pressures at increasing H_2 partial pressure and the dehydrogenation rate eventually became constant with an H_2 partial pressure higher than 58 kPa. There are two possible origins for the H_2 inhibition effect: 1) either the additional H_2 is reversing the C—H bond activation step by reacting with the formed alkyl group to re-form C_3H_8; or 2) it is increasing the H-content of the carbonaceous deposit and making it less willing to accept hydrogen from C_3H_8.

Example 6—Benchmark of PDH Activity on Different ZrO_2 Catalysts

A benchmark of the PDH reaction activity on different ZrO_2 catalysts was determined. The dehydrogenation rate of propane on ZrO_2 catalysts as prepared in Example 1 according to various embodiments was compared with the PDH activity data on ZrO_2 from previous studies (FIG. **8**). FIG. **8** shows a comparison of initial dehydrogenation rate of propane among ZrO_2 catalysts in current research: a) ZrO_{2c} dehydrogenation rate after the catalyst has been pretreated in 4 kPa O_2, He balance; b) the dehydrogenation rate after the catalyst been regenerated in 4 kPa O_2, He balance, and c) from references $ZrO_{2r\text{-}1}$, $ZrO_{2r\text{-}2}$ and $ZrO_{2r\text{-}3}$. The PDH reaction was operated with C_3H_8 at a pressure of 40 kPa and a temperature of 823K.

The ZrO catalysts from previous studies were commercial ZrO_2 (by Saint-Gobain) with different crystalline sizes (ZrO_2^r-1: 43 nm, ZrO_2^r-2: 13 nm, ZrO_2^r-3: 9 nm). The dehydrogenation rate at 823 K on the commercial ZrO_2 catalyst increased with decreasing crystalline size, but the selectivity towards propene decreased with decreasing crystalline size. For the ZrO_2^r-3 catalyst with a crystalline size of 9 nm, the selectivity towards propene was 98%. For the ZrO_2 catalyst as prepared in Example 1 according to embodiments herein, the dehydrogenation rate at 823 K was higher than that on ZrO_2^r-1 and the PDH reaction was highly selective towards propene (no contribution to cracking rate from ZrO_2 was observed after the subtraction of gas phase activity). After the PDH reaction, the ZrO_2 catalyst prepared in accordance with Example 1 and embodiments herein, was treated in 4 kPa O_2 at 823 K for 30 min and the subsequent PDH reaction after regeneration exhibited a dehydrogenation rate comparable with the first PDH activity measurement (FIG. **8**), which indicates the ZrO_2 catalyst can be fully regenerated by oxidative treatment. This observation is consistent with previous studies where several PDH reaction-regeneration cycles were performed on ZrO_2 at 823 K and no decrease in initial dehydrogenation rate was observed.

The introduction of additional H_2 during the PDH reaction on ZrO_2 catalyst provided a method to improve the stability of the catalyst through an inhibition of the formation of inactive carbonaceous species. This inhibition can lead to higher stability of the catalyst. No contribution to cracking rate from the ZrO_2 catalyst when additional H_2 was present during the PDH reaction at 873 K and all cracking products detected can be fully attributed to homogenous reactions that occur even in an empty reactor. This method may provide a general strategy to improve the stability of oxide-based catalyst during paraffin dehydrogenation reaction.

The preceding description sets forth numerous specific details such as examples of specific systems, components, methods, and so forth, in order to provide a good understanding of several embodiments of the present invention. It will be apparent to one skilled in the art, however, that at least some embodiments of the present invention may be practiced without these specific details. In other instances, well-known components or methods are not described in detail in order to avoid unnecessarily obscuring the present invention. Thus, the specific details set forth are exemplary. Particular embodiments may vary from these exemplary details and still be contemplated to be within the scope of the present invention.

Although the operations of the methods herein are described in a particular order, the order of the operations of each method may be altered so that certain operations may be performed in an inverse order or so that certain operation may be performed, at least in part, concurrently with other operations. In another embodiment, instructions or sub-operations of distinct operations may be in an intermittent and/or alternating manner.

It is to be understood that the above description is intended to be illustrative, and not restrictive. Many other embodiments will be apparent to those of skill in the art upon reading and understanding the above description. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

We claim:

1. A catalyst composition, comprising:

zirconium oxide (ZrO_2), wherein the catalyst composition is free of at least one of chromium or a precious metal, wherein the catalyst composition has been pretreated by contacting the catalyst composition with a pretreatment gas comprising a reducing agent at a concentra-

tion of about 1 mol % to about 10 mol %, and wherein the reducing agent comprises at least one of hydrogen (H_2), carbon monoxide (CO), ammonia or methane (CH_4).

2. The catalyst composition of claim **1**, comprising at least about 50 wt % ZrO_2 based on total weight of the catalyst composition.

3. The catalyst composition of claim **1**, comprising a plurality of Zr_{cus} surface-active sites.

4. The catalyst composition of claim **1**, wherein the ZrO_2 comprises at least one of a monoclinic phase of ZrO_2 or a tetragonal phase of ZrO_2.

5. The catalyst composition of claim **1**, comprising a BET surface area of about 1 $m^2\ g^{-1}$ to about 100 $m^2\ g^{-1}$.

6. The catalyst composition of claim **1**, further comprising a rare earth metal comprising at least one lanthanide metal, an oxide thereof or combinations thereof.

7. The catalyst composition of claim **1**, further comprising about 0.5 wt % to about 50 wt % of a rare earth metal comprising at least one of yttrium (Y), erbium (Er), cerium (Ce), dysprosium (Dy), gadolinium (Gd), lanthanum (La), neodymium (Nd), samarium (Sm), ytterbium (Yb), oxides thereof or mixtures thereof.

8. The catalyst composition of claim **1**, further comprising yttria, wherein an atomic ratio of Y:Zr is from greater than 0 to about 0.2.

9. The catalyst composition of claim **8**, comprising a BET surface area of about 40 $m^2\ g^{-1}$ to about 110 $m^2\ g^{-1}$.

10. The catalyst composition of claim **1**, wherein the catalyst composition has been pretreated and comprises more surface-active sites than before pretreatment.

11. The catalyst composition of claim **1**, comprising a plurality of units, wherein the plurality of units comprise at least one of particles, powder, extrudates, tablets, agglomerates, granules, spheres or combinations thereof.

12. The catalyst composition of claim **11**, wherein the plurality of units comprise a mean size of about 1.5 mm to about 5.0 mm.

13. The catalyst composition of claim **11**, wherein the plurality of units comprise a mean size of about 100 μm to about 250 μm.

14. A kit comprising:

a catalyst composition comprising zirconium oxide (ZrO_2), wherein the catalyst composition is free of at least one of chromium or a precious metal; and

at least one of:

(A) instructions for pretreating the catalyst composition, comprising:

contacting the catalyst composition with a pretreatment gas, wherein the pretreatment gas comprises a reducing agent at a concentration of about 1 mol % to about 10 mol %, and wherein the reducing agent comprises at least one of hydrogen (H_2), carbon monoxide (CO), ammonia or methane (CH_4); or

(B) instructions for using the catalyst composition, comprising:

dehydrogenating a light alkane gas, comprising combining hydrogen (H_2) with the light alkane gas in the presence of the catalyst composition.

15. A catalyst composition, comprising:

zirconium oxide (ZrO_2), wherein the catalyst composition is free of at least one of chromium or a precious metal, wherein the catalyst composition is in the form of a plurality of units, wherein the plurality of units comprise at least one of particles, powder, extrudates, tablets, agglomerates, granules, spheres or combinations thereof, and wherein the plurality of units comprise a mean size of about 1.5 mm to about 5.0 mm.

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